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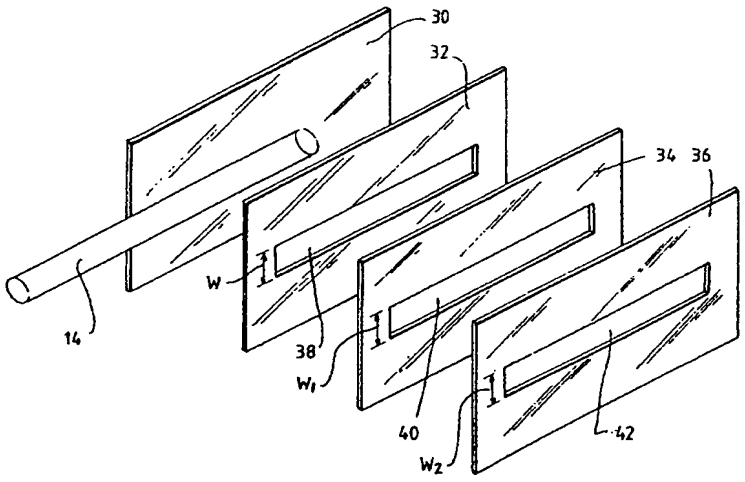
(54) Title: A TIME OF FLIGHT MASS SPECTROMETER INCLUDING AN ORTHOGONAL ACCELERATOR



(57) Abstract: A time of flight mass spectometer is disclosed which includes an ion source (10), an orthogonal accelerator (20), a reflectron (24) and a detector (22). The orthogonal accelerator (20) has a first electrode (32) which is a gridless electrode and includes a slot which is elongated in the direction of an ion beam supplied to the orthogonal accelerator from the source (10). The orthogonal accelerator (20) has a second thin plate electrode having a slot parallel to the slot in the first electrode and a third electrode with a slot parallel to the slot in the first electrode. The electrodes produce a retarding field during an ion accumulation mode, and an extraction field during an ion extraction mode.

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A TIME OF FLIGHT MASS SPECTROMETER INCLUDING AN ORTHOGONAL ACCELERATOR

This invention relates to a time of flight mass spectrometer including an orthogonal accelerator.

Time of flight mass spectrometers generally include an ion source for producing a continuous or pulsed beam of ions which are directed in a first direction. The ions generally pass through various electric focusing optics so as to collimate the beam and to direct the beam to an orthogonal accelerator. The orthogonal accelerator pushes ions in the ion beam out of the beam in a direction transverse to the first direction into a flight tube so that the ions travel along the tube and eventually arrive at a detector. The time taken to travel along the tube and arrive at the detector is dependant on the mass of the ions and therefore the detection of ions at different time intervals can provide an indication of the mass of the ions in the ion beam and therefore the material in the sample substance which is being analysed and from which the ion beam is formed.

Conventional orthogonal accelerators generally comprise a number of electrodes at least some of which are in the nature of grids. Electric potentials are applied to the various electrodes so as to force the ions to travel in the direction transverse to the first direction. The grid electrodes enables some of the ions to pass through the grid and therefore into the tube for detection at the detector.

The grids in conventional orthogonal accelerators produce a number of disadvantages including the fact that the grids become covered by deposits and may start charging up thus reducing mass peak stability, grids reduce sensitivity by absorbing part of the beam and scattering transmitted ions,

and grids are difficult to mount reproducably.

The present inventor has found that the main problem which grids cause is associated with the grid closest to the ion beam which enters the orthogonal accelerator. Ions have the lowest energy during accumulation in the acceleration stage and therefore even small voltages induced by charge contamination is enough to ruin the integrity of the beam entering the orthogonal accelerator. This charge contamination can result in an angular divergence of ions out of the beam as the beam enters into the orthogonal accelerator. The angular divergence induced by contamination results in greatly increased time of flight and geometrical aberrations which reduces a resolution of the spectrometer. The influence of deposits on further grids is orders of magnitude lower as those grids are shielded by the first grid and also ions possess much higher energies when they finally pass through those grids during the extraction process from the orthogonal accelerator.

The present invention may be said to reside in a time of flight mass spectrometer including:

means for producing a beam of ions and for directing the beam of ions in a first direction;

an orthogonal accelerator for receiving the beam of ions and for accelerating ions in the beam in a direction transverse to the first direction into a time of flight cavity;

a detector for detecting the ions after travel from the orthogonal accelerator through the time of flight cavity; and

wherein said orthogonal accelerator has;

a plurality of electrodes for receiving electric potentials, and for extracting ions in a direction transverse to the first direction, one of the electrodes being the first electrode through which ions are

transported during extraction of the ions in the transverse direction by the orthogonal accelerator; and

wherein the first electrode is a gridless electrode including a slot which is elongated in the said first direction.

According to the present invention the orthogonal accelerator can operate in two modes. The first of the two modes being an accumulation mode, in which inevitable stray and scattered ions are prevented from bleeding into the time of flight cavity by the field between the first electrode and another of the pluralities of electrodes while the beam stays far enough from the first electrode not to be perturbed by the electric field created by the first electrode; and the second mode being an extraction mode when fields on both sides of the first electrode change in such a way that the difference in field gradients is not high enough to introduce noticeable time of flight aberrations and angular scattering.

Preferably the width of the slot in the first electrode does not exceed the largest distance from the slot to any ion within the ion beam during the accumulation mode when ions are accumulated in the orthogonal accelerator prior to extraction in the transverse direction.

Preferably said first electrode forms together with further electrodes of the plurality of electrodes, a retarding field during the ion accumulation mode, and an extraction field during the ion extraction mode in such a way that minimum size of an ion packet of a given mass to charge ratio both in space and time of flight is achieved at the detector.

Preferably the orthogonal accelerator comprises;

a flat back plate electrode;

a thin plate electrode which forms said first

electrode, the flat back plate electrode and the thin plate electrode defining a space for receiving the ion beam which is directed in the first direction;

a thin-plate second electrode having a slot parallel to the slot in the first electrode;

a third electrode with a slot parallel to the slot in the first electrode; and

wherein electric potentials on all electrodes are variable independently, so that during the accumulation mode the voltage between the first and second electrodes is retarding for ions and during the extraction mode all voltages are changed in such a way that an extraction field is formed for accelerating the ions in the transverse direction.

Preferably the widths of the slots in the first and second electrodes are equal, and the gap between the back plate electrode and the first electrode is equal to the gap between the second and third electrodes, and the gap between the first and second electrodes being three times smaller than the gap between the thin plate second and third electrodes and two times bigger than the width of the slots in the first and second electrodes.

Preferably the time of flight spectrometer includes ion gating means, a reflectron and a lens, and wherein;

voltages applied during the extraction mode are chosen in such a way that non uniform electric fields provides both spacial and first or second order time of flight focusing exactly in the plane of the ion gating means;

the lens is elongated along the first direction and has voltages applied to it in such a way that minimum spacial size of ion packets is achieved at the detector; and

voltages on the reflectron are adjusted in such a way that minimum time of flights spread of ion packets is

achieved at the detector.

Preferably the ion beam in the first direction is directed into the space between the back plate electrode and the first electrode a minimum distance from the back plate electrode.

Preferred embodiments of the invention of the invention will be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 is a schematic diagram of a time of flight mass spectrometer;

Figure 2 is a schematic diagram showing the orthogonal accelerator according to the preferred embodiment of the invention;

Figures 3 and 4 are graph showing the application of electric potentials during the accumulation mode and extraction mode respectively for the embodiments shown in Figure 2;

Figure 5 is a view of a second embodiment of the invention;

Figure 6 and Figure 7 are graphs showing a graph of electric potential during an accumulation mode and extraction mode applicable to the embodiment shown in Figure 5; and

Figure 8 is a schematic perspective view of the orthogonal accelerator.

With reference to Figure 1, time of flight mass spectrometers are well known and therefore the schematic representation shown in Figure 1 is merely to provide a basic outline of the position of the orthogonal accelerator in the time of flight spectrometer. The spectrometer generally comprises an ion source 10 which may be an inductively coupled plasma ion source, an electro spray or the like. Generally focusing optics and beam creating optics 12 are provided for focusing and directing an ion

beam 14 from the source 10 in a first direction *x*. An orthogonal accelerator 20 is provided for accelerating the ion packets from the beam in a second direction *y* transverse to the direction *x* into a time of pulse tube or cavity. The ion packets accelerated from the orthogonal accelerator 20 may be received directly by a detector 22 or, as in the case of Figure 1, a reflection 24 may be provided for turning the ion packets 16 before they arrives at the detector 22. An ion gate 17 is disposed in the path of the ions for selectively filtering unwanted ions and a lens 18 is provided for focusing of the ions 16.

With reference to Figures 2 and 8 the orthogonal accelerator 20 most preferably comprises a flat back electrode 30 which is held at a static potential U0. A first electrode 32 forms a compensation electrode which is approximately 0.2 mm thick and which is spaced from the back electrode 30 by a distance of about 6 mm. A potential U1 is applied to the electrode 32. A second electrode 34 forms a pull out and electrode is spaced from the electrode 32 by a distance of about 4 mm and is about 0.2 mm thick. A potential U2 which is greater than the potential U1 (for positive ions) is applied to the electrode 34. A further 30 mm downstream from the electrode 34 is a third electrode 36 which forms an exit electrode U3 which is about 1 mm thick and is kept at the potential of the time of flight cavity or tube 23 (see Figure 1). The electrodes 32, 34 and 36 are gridless solid plate electrodes which have a slot 38, 40 and 42 respectively which is elongated in the direction of the beam 14 (i.e. direction *x*) from the ion source 10. The slot 38 has a width w (see Figure 8) of about 4 mm, and the slot 40 has a width of W_1 of about 3 mm.

The exit electrode 36 is also preferably gridless and has slot 42 which is also elongated in the direction of the ion beam 14. The width W_2 of the slot 42 is about 3 mm.

Typically, (U2-U1) is > (U0-U3)/100, so that virtually no fieled is experienced by ions moving near the back electrode 30, while ions penetrating through the slot 38 of the compensation electrode 32 experience a retarding field. This field stops ions bleeding into the time of flight tube or cavity 23 thus drastically reducing ion background.

During the extraction mode, a positive pulse P1 is applied to the back electrode 30 and a negative pulse of amplitude P2 is applied to the pull out electrode 34 less than 20 ns later. Amplitudes of the pules are related as P2=P1x(1.2-1.4) depending on beam divergence and position of the time of flight focus. Also, P2=(U0-U3)x0.2.

The electrode 32 provides as low as possible electric fields in the region of ion beam 14 during accumulation, absorbs some scattered ions and also serves as a filed-sustaining and focusing electrode during ion extraction.

A second embodiment is shown in Figures 5 to 7 in which the only difference to that described with reference to Figure 2 is a grid as attached to the pull out electrode 34 and thus the arrangement shown in Figure 5 may be regarded as inferior to that shown in Figure 2. However, the arrangement shown in Figure 5 allows the use of lower static voltages (U2-U1)>(U0-U3)/300 and allows easier tuning. In all modes and constructions, potential U1 is variable; | U1-U0 |>0.001x(U0-U3). The acceleration stage of the orthogonal accelerator in both Figures 1 and Figure 2 may also be combined with ion gating (eg. flat deflection plates activated by short electric pulses) at the plane of the time of flight focusing. In this case, potentials P1, P2 and U1 could be tuned to provide simultaneous second-order focusing on the time of flight as well as spacial focusing. The later allows to improve mass resolution of the ion gating means.

The deflection of the ion beam during the accumulation mode is minimised by choosing the width of the slot in the compensation electrode 32 small compared to the distance from the slot 2 ions in the beam 14. However, this slot 38 should be big enough to allow all ions of the beam to pass through during the subsequent extraction mode. It has been found experimentally that in such a construction contamination from the ion beam is absorbed mainly by electrodes downstream of the compensation electrode 32 and therefore influences of contamination on the ion beam is greatly reduced.

Preferably all of the electrodes 30, 32, 34 and 36 are formed from non-magnetic stainless steel.

In other embodiments the speedometer may include ion trapping or collisional cooling or additional focusing/deflecting ion optics before the orthogonal accelerator.

The slots in the electrodes 32, 34 and 36 could be formed by electroetching, electroforming or laser cutting

In some embodiments of the invention a slotted plated electrode is located between the first electrode 32 and the back electrode 30 to assist in confining the electric fields produced by the electrodes 32, 34 and 36. This plate electrode does not play any part in the ion beam formation and is usually at the potential of the back plate electrode 30 or another electrode to which it is connected.

In other embodiments first interfaces may be utilised between the ion source and the orthogonal accelerator 20 including collisional cooling or chemical reactions in RF multipoles at elevated pressures, MS-MS stages and additional ionoptics. More than one reflectron or additional lenses may also be utilised within the time of

flight cavity 23. Furthermore, the orthogonal accelerator 20 could omit the electrode 36 (and therefore be a two-stage orthogonal accelerator, or electrode 32 may be pulsed (e.g. instead of the electrode 34).

Ion sources include the ICP electrode as described, or ES, APCI, EI-CI-MALDI sources.

Since modification within the spirit and scope of the intention may readily be effected by persons skilled within the art, it is to be understood that this invention is not limited to the particular embodiments described by way of example hereinabove.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A time of flight mass spectrometer including:

means for producing a beam of ions and for directing the beam of ions in a first direction;

an orthogonal accelerator for receiving the beam of ions and for accelerating ions in the beam in a direction transverse to the first direction into a time of flight cavity;

a detector for detecting the ions after travel from the orthogonal accelerator through the time of flight cavity; and

wherein said orthogonal accelerator has;

a plurality of electrodes for receiving electric potentials, and for extracting ions in a direction transverse to the first direction, one of the electrodes being the first electrode through which ions are transported during extraction of the ions in the transverse direction by the orthogonal accelerator; and

wherein the first electrode is a gridless electrode including a slot which is elongated in the said first direction.

2. The spectrometer of claim 1 wherein the width of the slot in the first electrode does not exceed the largest distance from the slot to any ion within the ion beam during the accumulation mode when ions are accumulated in the orthogonal accelerator prior to extraction in the transverse direction.

3. The spectrometer of claim 1 wherein said first electrode forms together with further electrodes of the plurality of electrodes, a retarding field during the ion accumulation mode, and an extraction field during the ion extraction mode in such a way that minimum size of an ion packet of a given mass to charge ratio both in space and time of flight is achieved at the detector.

4. The spectrometer of claim 1 wherein the orthogonal accelerator comprises;

a flat back plate electrode;

a thin plate electrode which forms said first electrode, the flat back plate electrode and the thin plate electrode defining a space for receiving the ion beam which is directed in the first direction;

a thin-plate second electrode having a slot parallel to the slot in the first electrode;

a third electrode with a slot parallel to the slot in the first electrode; and

wherein electric potentials on all electrodes are variable independently, so that during the accumulation mode the voltage between the first and second electrodes is retarding for ions and during the extraction mode all voltages are changed in such a way that an extraction field is formed for accelerating the ions in the transverse direction.

5. The spectrometer of claim 1 wherein the widths of the slots in the first and second electrodes are equal, and the gap between the back plate electrode and the first electrode is equal to the gap between the second and third electrodes, and the gap between the first and second electrodes being three times smaller than the gap between the thin plate second and third electrodes and two times bigger than the width of the slots in the first and second electrodes.

6. The spectrometer of claim 1 wherein the time of flight spectrometer includes ion gating means, a reflectron and a lens, and wherein;

voltages applied during the extraction mode are chosen in such a way that non uniform electric fields provides both spacial and first or second order time of flight focusing exactly in the plane of the ion gating means;

the lens is elongated along the first direction and has voltages applied to it in such a way that minimum spacial size of ion packets is achieved at the detector; and

voltages on the reflectron are adjusted in such a way that minimum time of flights spread of ion packets is achieved at the detector.

7. The spectrometer of claim 1 wherein the ion beam in the first direction is directed into the space between the back plate electrode and the first electrode a minimum distance from the back plate electrode.

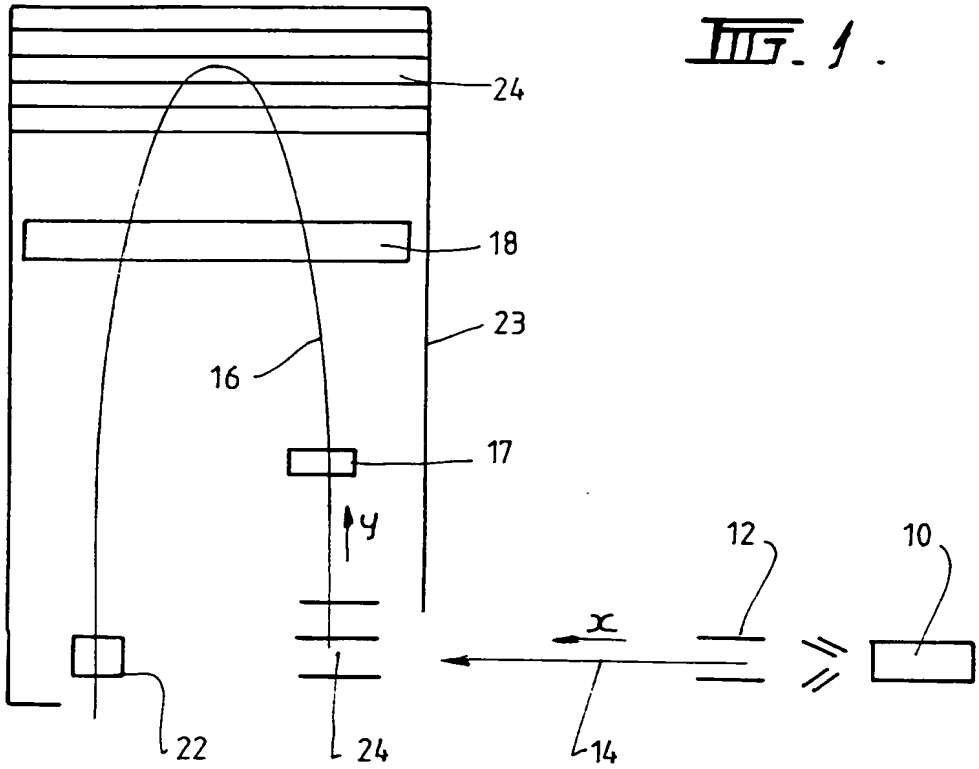

FIG. 1.

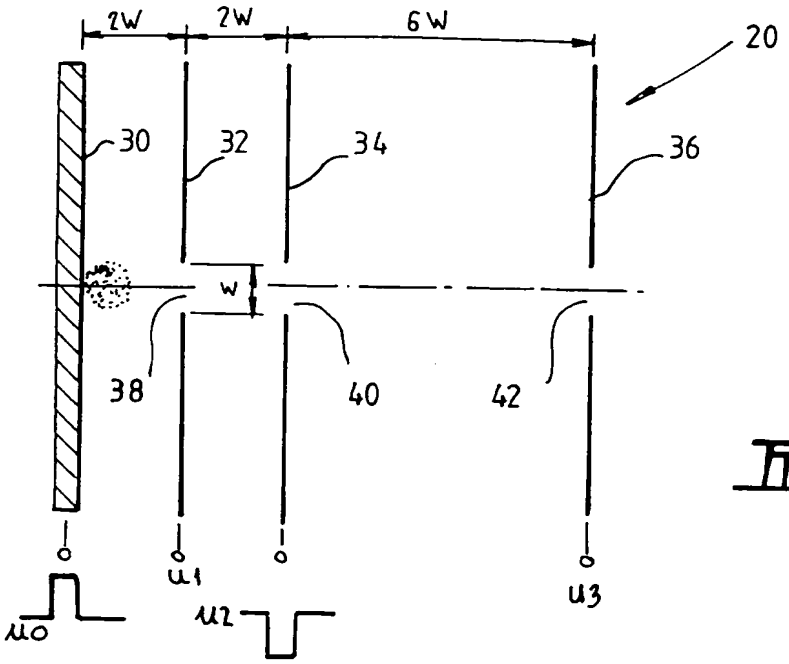

FIG. 2.

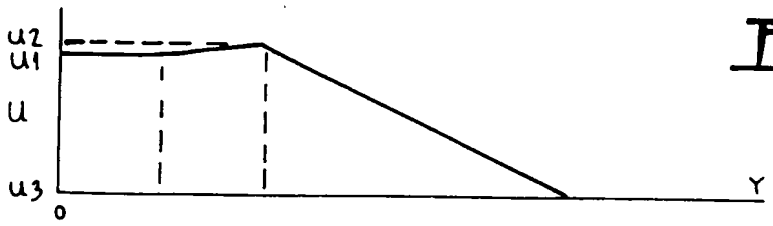

FIG. 3.

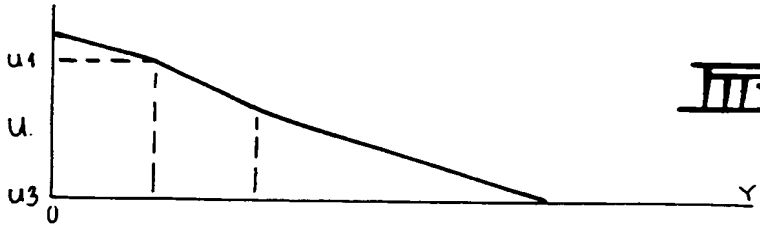

FIG. 4.

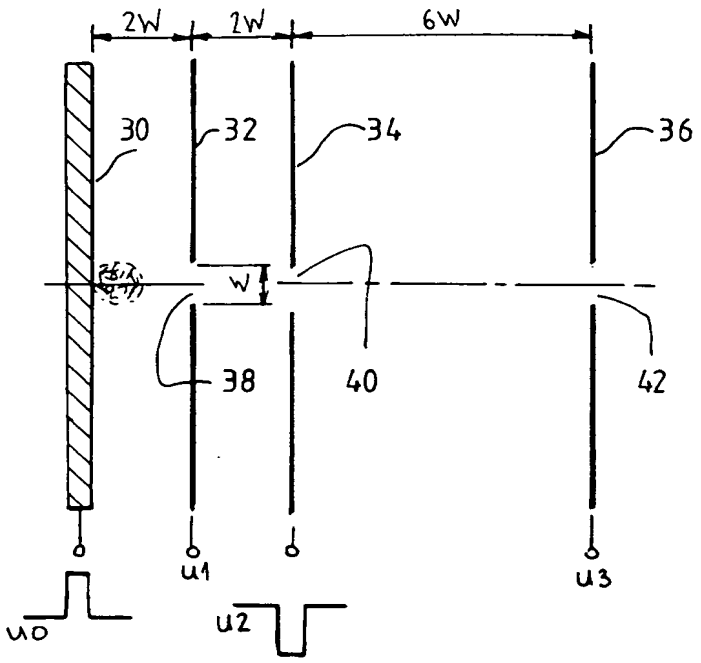

FIG. 5.

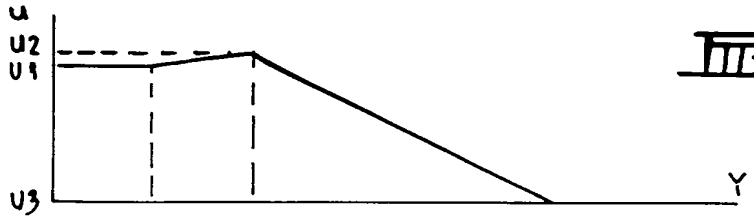

FIG. 6.

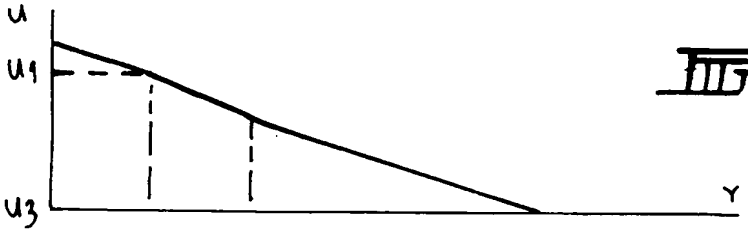

FIG. 7.

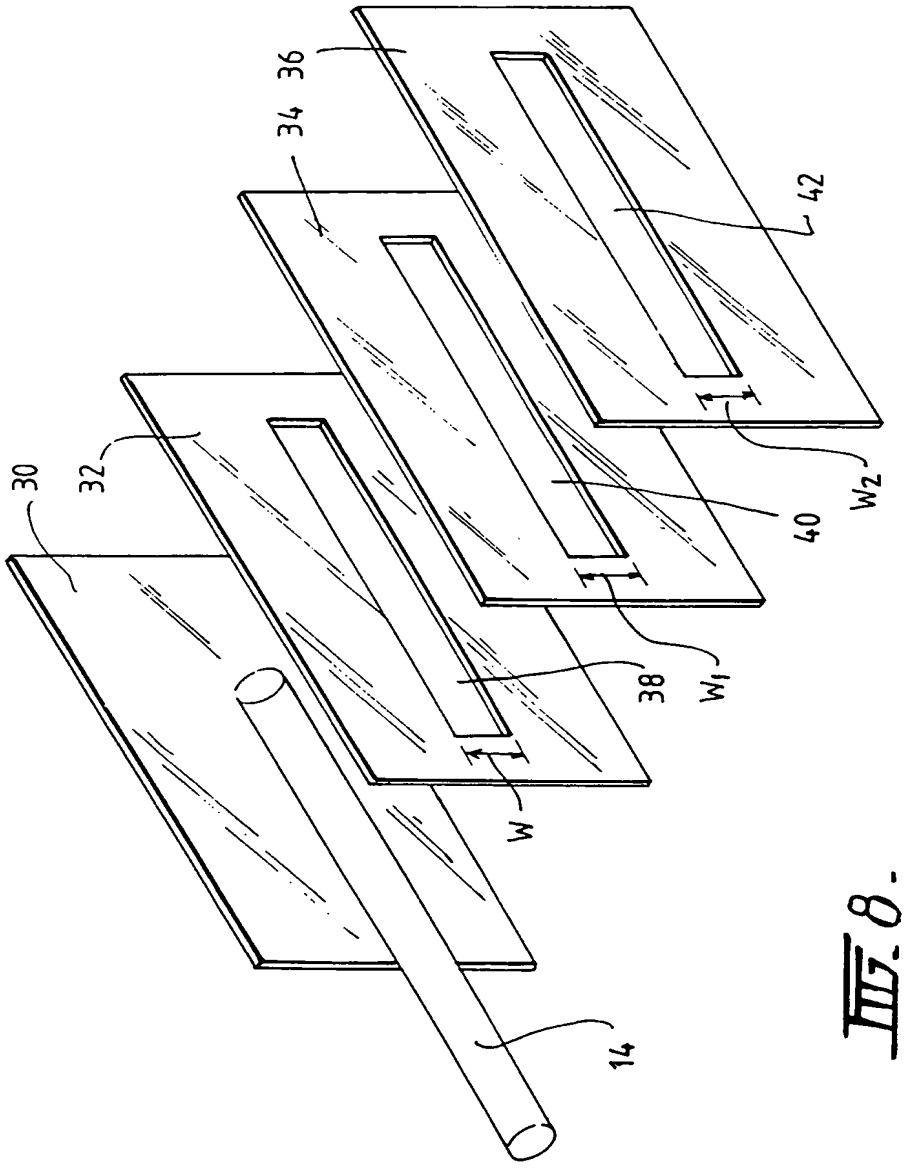

FIG. 8.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00922

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: H01J 49/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT and JAPIO with key-words: 'time of flight', TOF, gridless, slot, electrode, orthogonal, accelerator

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 97/48120 A (HD TECHNOLOGIES LIMITED) 18 December 1997 page 4 line 18 to page 5 line 3, page 6 line 14 to page 7 line 19, figure 1 page 7 lines 10 to 18, figure 1	1 - 3, 7 4 - 6
Y	US 5 464 985 A (CORNISH & COTTER) 7 November 1995 columns 5 and 8 to 11	4 - 6

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

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Date of the actual completion of the international search	Date of mailing of the international search report
6 November 2000	10 NOV 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorised officer **Ross Burdon** Telephone No : (02) 6283

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00922

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
WO	97/48120	AU	30411/97	GB	9612091
US	5 464 985		- none -		

END OF ANNEX